

Review

Combining non-thermal plasma with heterogeneous catalysis in waste gas treatment: A review

Jim Van Durme^a, Jo Dewulf^{a,*}, Christophe Leys^b, Herman Van Langenhove^a^a Research Group EnVOC, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium^b Department of Applied Physics, Faculty of Engineering, Ghent University, Rozier 44, B-9000 Ghent, Belgium

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Abstract

Plasma driven catalysis is a promising technology for waste gas treatment characterized by higher energy efficiencies, high mineralization rates and low by-product formation. The combination of heterogeneous catalysts with non-thermal plasma can be operated in two configurations: positioning the catalyst in the discharge zone (in-plasma catalysis) or downflow the discharge zone (post plasma catalysis).

In a first part of the review, changes of plasma properties resulting from the introduction of catalyst material are discussed. It has been reported that discharge types can even change. Accordingly, it was reported that microdischarges are formed within the catalyst pores. Changing plasma characteristics can eventually result in enhanced production of new active species, increasing the oxidizing power of the plasma discharge.

In a second part, it is discussed that plasma discharges also affect catalyst properties such as a change in chemical composition, enhancement in surface area or change of catalytic structure. These phenomena partially explain why catalyst adsorption kinetics of airborne pollutants are affected when exposed to plasma discharges.

It is also reviewed that the synergy of combining plasma with catalysts can not only be attributed to the production of new reactive species. Also plasma photon emission or thermal hot-spots can initiate catalytic pollutant oxidation reactions.

To conclude, an overview of recently published manuscripts concerning plasma catalysis for volatile organic compounds abatement is given. It is also discussed why heterogeneous plasma catalysis has high potential for the simultaneous abatement of NO_x and hydrocarbons.

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* Corresponding author. Tel.: +32 264 59 49; fax: +32 9 264 62 43.

E-mail address: jo.dewulf@ugent.be (J. Dewulf).

1. Introduction

The emission of volatile organic compounds (VOC) and NO_x by various industrial and agricultural processes is an important source of air pollution and, therefore, a problem for human health and the environment in general [1,2]. The United States Environmental Protection Agency (US EPA) has mandated NO_x emission reductions of 90–95% from current levels, starting in 2007 and phasing in completely by 2010. Well established technologies for VOC abatement are thermal and catalytic incineration, adsorption, condensation, biofiltration, membrane separation or ultra-violet oxidation [3,4]. For NO_x abatement processes, active lean NO_x catalysts, urea-selective catalytic reduction or lean NO_x trap catalysis has been used [5]. However, the severe emission tolerances are often difficult to handle using these conventional technologies [6]. Therefore, innovative research in the field of air purification becomes more and more important [4]. Extensive research has been done on using non-thermal plasma (NTP) as a technology for environmental protection, in particular as abatement technology for airborne hazardous compounds [7,8]. Non-thermal plasma typically consists of electrons which are accelerated by an electric field, gaining typical temperatures in the range of 10,000–250,000 K (1–25 eV), and which are not in thermal equilibrium with other particles. Electron–molecule collisions with bulk gas molecules (N_2 , O_2 , H_2O) result in the production of excited bulk gas molecules (e.g. N_2^*). Excited molecules lose their excess of energy by emitting photons or heat. The unstable reactive species (ions and radicals) are formed by dissociative electron attachment processes. Hydroxyl radicals result from water dissociation reactions, also producing hydrogen radicals which are, in oxygen-rich environments, scavenged and converted into HO_2^\bullet almost instantaneously [9]. VOC removal is generally attributed to radical reactions initiated by the attack of these O or OH radicals [10,11]. However, depending on the reaction conditions, other radical and ionic reactions also result in VOC conversion to CO_2 , H_2O and other degradation products [12,13].

Today, VOC abatement technology is most useful for moderate gas flow rates containing low VOC concentrations. Urashima and Chang [14] compared the economical application range of NTP processes with other chemical methods for the effective treatment (removal or conversion) of VOC. From their results, the applicable range of electrical discharges is about 0.01–1000 ($\text{N m}^3 \text{ h}^{-1}$) and 1–10,000 ppm_v , similar conclusions were made by Lu et al. [4]. Although NTP applications as end-of-pipe technology for the removal of VOC, SO_2 , H_2S and NO_x are frequently reported [15], it is seldom used due to site-specific constraints such as energy inefficiencies, poor mineralization, and by-product formation. One of the main problems of NTP technology is by-product formation such as a high CO formation. Magureanu et al. [16] reported that during trichloroethylene removal experiments, NTP gives CO_2 selectivities lower than 25%, while the major reaction product was CO with selectivities up to 70%. Van Durme et al. [17] detected

several higher hydrocarbons in the effluent gas during NTP toluene removal experiments including formic acid, benzaldehyde, benzyl alcohol, methyl-nitrophenols, Recent developments in NTP research focus on generating more oxygen active species to further oxidize CO into CO_2 molecules, eventually leading to a higher CO_2 selectivity [18]. The generation and stable operation of atmospheric non-thermal plasmas remains a challenge for modern plasma science and technology [19]. Next, conventional plasma technology often proves not to be competitive in both removal efficiency as in overall cost. The latter is determined by production costs and life span combined with the energy consumption [19].

A more effective use of plasma is possible by exploiting its inherent synergetic potential through combination with heterogeneous catalysts [8,20,21]. In the field of air purification, plasma driven catalytic technology has high potential as can be seen by increased mineralization efficiencies. Wallis et al. [22] measured no CO_2 during the destruction of 500 ppm_v dichloromethane when using only plasma. However, when $\gamma\text{-Al}_2\text{O}_3$ was introduced in the plasma discharge, CO_2 outlet concentrations were 32 ppm_v proving an increased mineralization rate. It can be concluded that by-product formation, such as aerosols, ozone and smaller organic compounds, is strongly reduced when using hybrid plasma catalyst technology [12]. Van Durme et al. [17] also reported that the energy efficiency for toluene degradation strongly increases using TiO_2 as in-plasma catalyst. Indeed, for dry air and an energy density of 17 J L^{-1} , adding 15 g TiO_2 increased the toluene ($C_{in} = 0.5 \text{ ppm}_v$) removal rate from 27 ± 4 to $82 \pm 2\%$. Similarly, introducing 15 g $\text{MnO}_2\text{-CuO/TiO}_2$ downstream the plasma discharge, resulted in 78% toluene removal efficiency for an energy density of 2.5 J L^{-1} , while this was only 2% in the absence of a catalyst.

Based on recent papers (2004–2007) the different mechanisms occurring in-plasma/catalyst hybrid configurations are reviewed. In a first part of this review it is shown that some authors report heterogeneous catalysts to affect plasma characteristics, while others claim that NTP initiate and influence catalyst mediated reactions. Secondly, the state-of-the art of plasma/catalyst combined systems in the field of waste gas treatment is presented.

2. Plasma catalytic mechanisms

Heterogeneous catalyst can be combined with NTP in two ways: by introducing the catalyst in the discharge zone (in-plasma catalysis, IPC) or by placing the catalyst after the discharge zone (post plasma catalysis, PPC) (Fig. 1a and b) [2,15]. For both IPC as PPC configuration, heterogeneous catalyst material can be introduced into the reactor in several ways (Fig. 1c): as coating on the reactor wall or electrodes, as a packed-bed (granulates, coated fibers, pellets) or as a layer of catalyst material (powder, pellet, granulates, coated fiber). In both designs many catalyst formulations have been proposed and tested. Reported in-plasma catalysts are BaTiO_3 , Al_2O_3 , SiO_2 , TiO_2 , MnO_2 and their derivatives (Table 1) [23]. Wallis

Table 1
Overview of recently published papers on plasma catalysis

Plasma type	VOC	Flow rate (mL/min)	Concentration range (ppm)	Catalyst	Position	Maximum removal efficiency (%)	Energy cost (g/kWh)	Ref.
DBD	Toluene	315	240	MnO ₂ /Al ₂ O ₃ MnO/AC Fe ₂ O ₃ /MnO ₂	IPC IPC IPC	55	11	[26]
Corona	<i>n</i> -Heptane			TiO ₂	IPC	50.4		[27]
DBD	Toluene Ammonia	667 × 10 ³	10–50	CuO/MnO ₂	PPC	50		[28]
DBD	Toluene	100–500	50	MnO ₂ /Al/Ni	IPC	>95	1	[20]
DBD	Benzene	250	300–380	TiO ₂ MnO ₂	IPC IPC	16	3 4	[4]
Corona (pulsed)	Toluene Benzene Hexane Methane	100	300	AlO ₂ Silica gel	IPC IPC	>95 75 25 5	156	[10]
DBD	SF ₆ NF ₃ CF ₄ C ₂ F ₆	600	300	CuO/ZnO/MgO/ Al ₂ O ₃	IPC IPC IPC IPC	>99 >99 66 83		[29]
DBD	Benzene Toluene <i>o</i> , <i>m</i> , <i>p</i> -Xylene Formic acid	4000	75–110	Ag/TiO ₂	IPC IPC IPC IPC	96	11	[12]
DBD	Toluene	500	250 100	MnO _x /CoO _x	IPC	>99 >99	2 1	[2]
Coil type (AC)	Benzene	4000–10,000	200	Ag/TiO ₂ Ni/TiO ₂ Ag/Al ₂ O ₃ Pt/Al ₂ O ₃ Pd/Al ₂ O ₃ Ferrierite Ag/H-Y	IPC IPC IPC IPC IPC IPC IPC	>99 >99 >99 >99 >99 >99 >99	10	[7]
DBD	Formaldehyde	605	140	Ag/CeO ₂	IPC	92	6	[30]
DC positive corona	TCE	1500	100	TiO ₂	IPC	85	3	[31]
Streamer	Toluene	133 × 10 ³	45	CuOMnO ₂ /Al ₂ O ₃	PPC	96	33	[21]
DC positive corona	Toluene	10,000	0.5	CuOMnO ₂ /Al ₂ O ₃ TiO ₂	PPC IPC	>99 >99		[11]
Coil type (AC)	Toluene	500	200	Zeolites	IPC (discontinue)			[32]
Dielectric pellet-bed reactor	CFC-12	1000	500	TiO ₂	IPC	27	36	[24]
DBD	Isopropanol	500	250	MnO _x /CoO _x	IPC	>100	9	[33]
DBD	Trichloroethylene	510	430	Au/SBA-15	PPC	>99		[34]
DBD	Trichloroethylene	500	250	MnO ₂	PPC	97		[35]
DBD	Dichloromethane	1000	500	γ-Al ₂ O ₃ α-Al ₂ O ₃ TiO ₂ HZSM-5 NaZSM-5 NaA NaX	IPC/PPC PPC PPC PPC PPC PPC PPC	51/43 34 39 41 38 37 40		[36]

et al. [24] demonstrated that a variety of catalysts which were originally investigated in the field of thermal catalysis show similar synergy when combined with NTP. These kind of catalysts include platinum-based catalysts [25], protonic zeolites, modified Y-zeolites, de-aluminated Y-zeolites, NaX and NaY zeolites, HZSM-5-supported manganese oxides and

LaCoO₃. From recent publications it can be considered that the mentioned catalyst materials are also used in PPC configuration. However, Table 1 illustrates that in recent years most attention is given to IPC, particularly dielectric barrier discharge (DBD) packed-bed reactors are frequently used for experimental research.

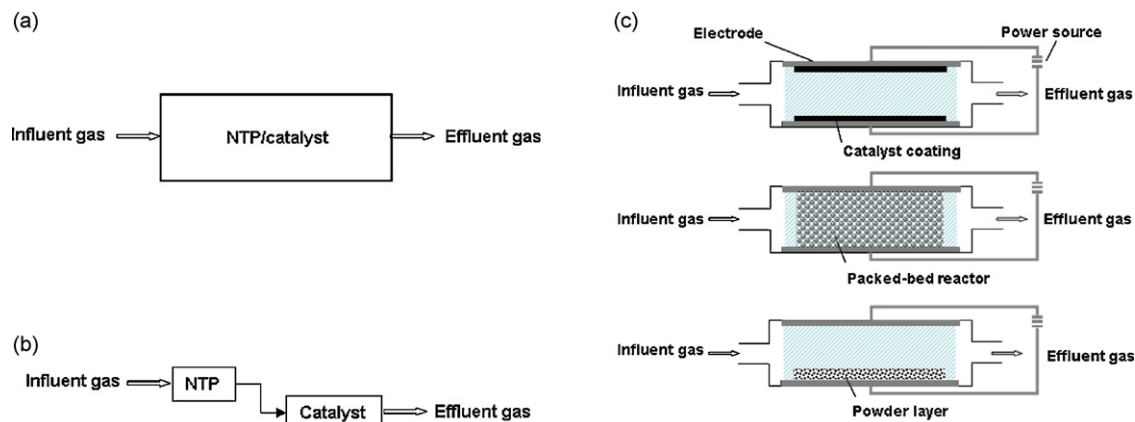


Fig. 1. Schematic overview of two plasma-catalyst hybrid configurations; (a) in-plasma configuration (IPC) and (b) post plasma configuration (PPC). The most common catalyst insertion methods are summarized for IPC configuration (c).

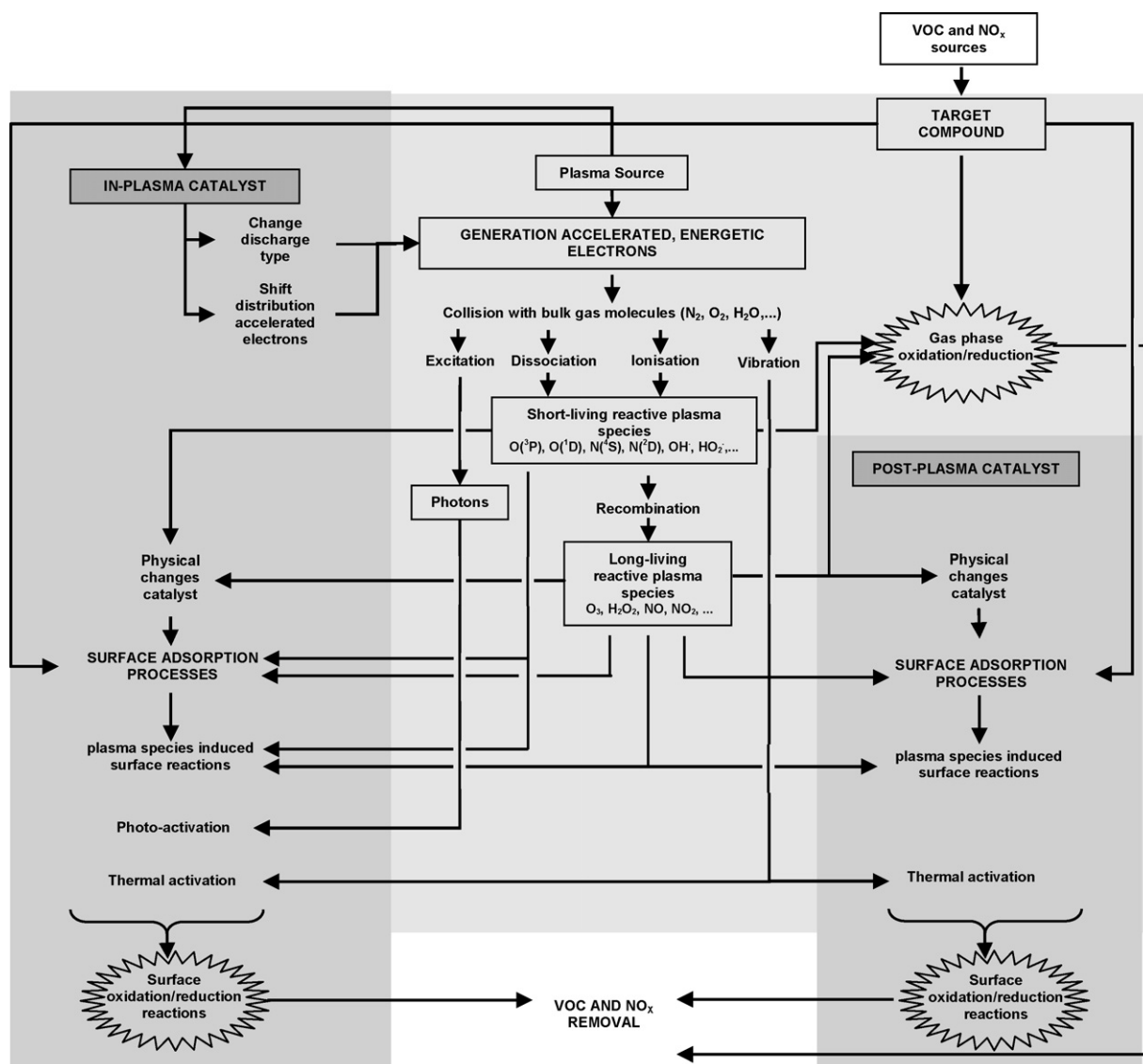


Fig. 2. Schematic summary of plasma catalytic phenomena.

Fig. 2 summarizes several plasma driven catalytic processes which will be discussed in more detail during this review. It can be seen that introducing catalysts into the plasma discharge may affect the type of discharge or can induce a shift in the distribution of the accelerated electrons. These processes again influence the production of excited and short-living reactive plasma species. New reactive species (e.g. atomic oxygen, superoxide species (O_2^-), hydroxyl radicals, ...) can also be generated during the IPC process. Not only short-living unstable reactive species are produced in plasma discharges, a fraction recombines to form more stable species (e.g. ozone). Since these species have higher lifetimes, they are able to reach catalyst material positioned downstream the discharge zone (PPC). The presence of highly reactive plasma species and electrons trigger physical changes of the catalyst material and consequently affect VOC surface adsorption. Plasma driven catalytic systems show zeroth-order kinetics, indicating the important role of surface reactions during VOC decomposition. Accordingly, Kim et al. [12] reported that while VOCs with low ionization potentials usually have higher oxidation efficiencies in gas-phase NTP, this relationship is not observed in NTP-catalyst hybrid systems. Again, this proves that VOC decomposition is mainly influenced by adsorption processes, rather than by discharge characteristics. From Fig. 2 it is clear that gas temperature increase during plasma operation is able to thermally activate catalyst materials. Catalyst activation is also feasible by photon irradiation.

To conclude, several processes are possible when catalysts are combined with non-thermal plasmas. Overall, it can be postulated that VOC removal becomes more efficient and higher mineralization rates, indeed Van Durme et al. [17] reported that the energy efficiency of combining NTP with $CuOMnO_2/TiO_2$ in downstream position resulted in a toluene degradation energy efficiency of 1.06 g kWh^{-1} which was around 35 times higher than with plasma alone (0.03 g kWh^{-1}). In this study it was also illustrated what the effect of hybrid plasma catalysis was on by-product formation such as ozone (Fig. 3).

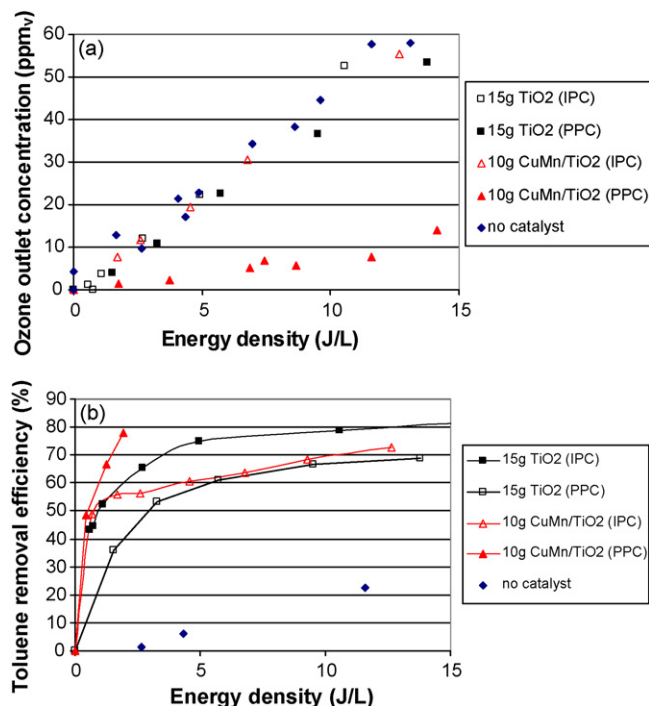


Fig. 3. Different hybrid plasma catalyst configurations (IPC vs. PPC) for Aerolyst[®] 7706 TiO_2 and $CuOMnO_2/TiO_2$ catalysts; effect on (a) ozone outlet concentration (ppm_v) and (b) toluene removal efficiency (%) as a function of energy density ($J L^{-1}$) [11].

2.1. Physical–chemical effects during plasma catalytic processes

Malik et al. [10] wrote that in most of the research papers on plasma catalytic hybrid systems, the focus is put on catalytic reactions, whereas the adsorption processes at the catalyst surface has received less attention. Recent papers indicate that combining catalysts with NTP may result in physical–chemical changes such as a shift of mean electron energy, change of discharge type, effect on catalyst properties or an impact on the VOC adsorption process (Fig. 2) [8,10,37].

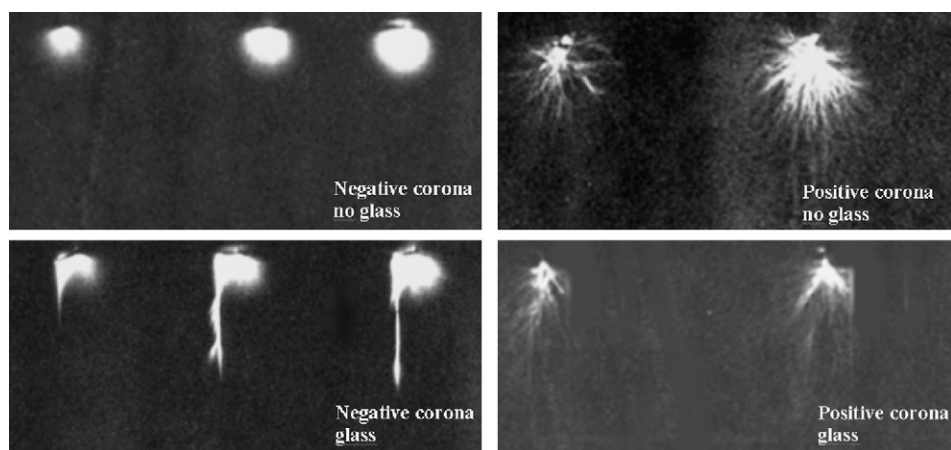


Fig. 4. Photographs of the discharge under negative and positive polarities, respectively, with glass displaced 10 mm laterally from the high voltage electrode [39].

2.1.1. Physical–chemical effects of catalysts on plasma properties

2.1.1.1. Change of discharge type and shift in distribution of accelerated electrons. The influence of changing the discharge type from streamers in air alone to streamers along insulator surfaces (surface flashover) has recently been described in literature [10]. It is known that plasma streamers travel along insulators (Fig. 4) [38], showing enhanced ionization compared to streamers in the gas space. As a consequence it is expected that VOC oxidation near insulators will be enhanced. In the presence of additional surface provided by heterogeneous catalysts, a similar effect has been noticed [10]. Rodrigo et al. [39] reported that corona interaction is the highest when surface is in direct contact with the electrode at which the corona originates. Indeed, it can be seen on Fig. 4 that a glass surface, displaced 10 mm laterally from the electrode, enhances the propagation of the corona under negative polarity, but inhibits propagation with the positive polarity case [39]. Next, Hensel et al. [40] and Holzer et al. [15] reported that microdischarges might be generated inside the catalyst pores, resulting in more discharge per volume and increasing the mean energy density of the discharge. In addition, it has been reported that inserting ferroelectric materials in the plasma induces a shift in accelerated electron distribution. This phenomenon can be attributed to an increased electric field with a factor of 10–250, leading to a more oxidative plasma discharge [15]. Similar conclusions were made for in-plasma zeolites [41] which easily interact with discharge plasmas due to a very strong natural electric field within their framework.

2.1.1.2. Generation of new reactive species. Introducing heterogeneous catalysts in the plasma discharge may increase the production of active species. This phenomenon was supported by Roland et al. [8] who studied the oxidation mechanism of various organic substances immobilized on non-porous and porous carriers and concluded that these short-living oxidizing species are formed in the pore volume of porous materials when exposed to NTP. Also, Chavadey et al. [42] found that insertion of TiO_2 in the discharge zone contributed to an acceleration of the superoxide radical anion (O_2^-) formation, consequently inhibiting recombination processes and increasing the total catalytic activity. Plasma

generates intermediate species having a sufficiently long lifetime to trigger surface reactions on a catalyst placed downflow the plasma reactor [43]. Short-living oxidizing species cannot reach this post plasma catalyst [2]. It is clear that mainly ozone is decomposed catalytically, forming molecular and highly active atomic oxygen [21,24,44]. This phenomenon is described for a number of catalysts such as silica gel, porous alumina and metal oxides [8,11]. Lewis acid sites often appear to play a major role in the catalytic process. Sample pretreatment (e.g. calcinations temperature and residual water content) as well as the presence of additives and impurities influence the activity for ozone decomposition [8].

2.1.2. Physical–chemical effects of plasma on catalyst material

2.1.2.1. Effect on catalyst properties. Non-thermal plasma has been used in a series of surface treatment applications throughout the last few decades [45]. This indicates that during plasma operation, catalyst surfaces might be affected in three different ways. First, discharges may enhance the dispersion of active catalytic components [20]. NTP proved to influence the stability and catalytic activity of the exposed catalyst materials. Secondly, the oxidation state of the material can be influenced when exposed to plasma discharge [8,20,24,37,46]. To support this, a Mn_2O_3 catalyst was exposed to a non-thermal plasma (energy density of 756 J L^{-1}) for 40 h. After this experiment Mn_3O_4 was detected, this lower-valent manganese oxide is known to have a larger oxidation capability [20]. Similarly, Wallis et al. [24] reported that due to plasma catalyst interactions, less parent Ti–O bonds are found on TiO_2 surfaces. Pribytkov et al. [37] and Jun et al. [46] both agreed that in hybrid plasma catalyst configurations new types of active sites with unusual and valuable catalytic properties may be formed. Similar conclusions were taken by Roland et al. [8] who observed stable $\text{Al}_2\text{O}_3\text{O}^*$ paramagnetic species formation (lifetime >14 days). These were formed during Al_2O_3 IPC experiments at the interior of the pores by direct plasma processes (electrons, UV, plasma species such as OH, OD, ...). Finally, it was postulated that plasma exposure could even result in an specific surface area enhancement or in a change of catalytic structure [20]. Indeed, Fig. 5 compares SEM images of manganese oxide/alumina/nickel foam before and after DBD

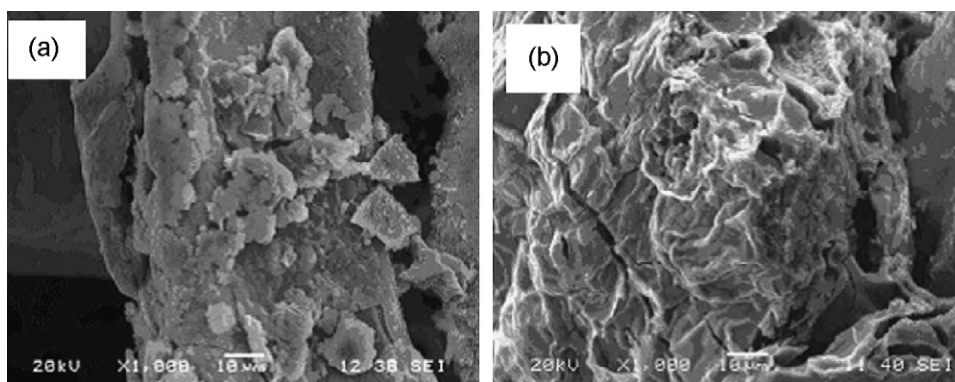


Fig. 5. SEM images of manganese oxide/alumina/nickel foam before/after DBD reaction (1000×) (a) before and (b) after DBD exposure [20].

reaction. It was found that the granularity of the grain on the catalyst surface becomes smaller and the distribution is more uniform after discharge exposure. This results in the formation of ultrafine particles with higher specific surface and less-perfect crystal lattice having a large number of vacancies [20]. These physical changes induce a higher catalytic activity, partially explaining the synergetic effect of plasma catalytic systems [8,20]. Contrary, Wallis et al. [22] reported that BET surface areas can be reduced after plasma exposure: in the case of HZSM-5 (zeolite catalyst) a reduction of about 45% was measured while this was only about 6% for TiO₂ catalysts.

2.1.2.2. Effect on adsorption process. Adsorption processes are strongly influencing the efficiency of plasma catalytic driven processes. A strong adsorption of the sorbate (VOC) combined with a large adsorption capacity of the sorbent is a prerequisite for a high performance of plasma-assisted catalysis used as air cleaning technology. Kwak et al. [47] proved that differences in the amount and strength of NO₂ adsorption on Na-Y zeolites, mainly determine the NO_x removal efficiency. Lin et al. [48] reported that the ionic wind may enhance plasma catalytic removal by increasing adsorption. Kinetic models commonly used in literature to study VOC surface oxidation corresponds to three types: Langmuir–Hinshelwood (LH), Eley–Rideal (ER) and Mars–van-Krevelen (MVK) [49]. LH models consider that the reaction takes place between both reactants adsorbed on the catalyst surface. ER mechanisms consider that the reaction takes place between one adsorbed reactant and the second reactant in the boundary layer. According to MVK models, the reaction takes place through alternative oxidations and reductions of the catalyst surface, the surface oxidation being produced by molecular oxygen [49]. Blin-Simiand et al. [50] reported that the adsorption–desorption equilibrium of the molecule at surfaces is greatly influenced by the plasma discharge. In the case of interaction between adsorbed molecules and polar surfaces, electrostatic forces are more important than Van Der Waals forces. This effect can be quantified by the so-called parameter of specific interaction of polar solutes [51]. This parameter involves the surface properties in terms of potential and acid–base interactions, and includes different interactions (physical or electric) between molecules, such as Keesom and Debye interaction or hydrogen bonding [49].

2.1.2.3. Thermal activation of catalyst. During non-thermal plasma operation, ambient gas temperatures increase due to inelastic electron–molecule collisions. Consequently, higher catalyst surface temperatures are often measured in hybrid plasma catalyst configurations [4]. Ambient gas temperatures in non-thermal plasmas are determined by the gas mixture, gas residence time or type of discharge reactor. Hammer et al. [43] measured that for a specific input energy density of 10 J L⁻¹, gas temperature in DBD discharges increase roughly 10–15 °C. Other papers reported a temperature increase of approximately 70 °C at 200 J L⁻¹ [7]. In a more detailed study by Staack et al. [52] this effect was explained by an increase in rotational temperature with discharge current and electrode spacing. The

vibrational temperature decreases with increasing rotational temperature and also decreases at low discharge currents and smaller electrode spacing. This results in an optimal regime for creating vibrationally excited species. This explains why gas temperature typically increases with discharge current and then levels off.

However, it has to be mentioned that the macroscopic gas temperature is often too moderate to explain thermal catalytic activation [15]. This indicates that hot spots can be formed on the catalyst surface. These hot spots are rather small zones which were equally distributed within the catalyst bed. These active volumes are presumably formed by strong micro-discharges appearing in particular between sharp edges and corners of adjacent pellets. Because ions and neutrals still have much lower temperatures compared to the accelerated electrons, the used discharges are still of the non-thermal plasma type. It has been proven that these increased catalyst temperatures promote catalytic VOC removal. This effect has been described by Kim et al. [7] during benzene degradation experiments with Pt/Al₂O₃ catalyst. Holzer et al. [15] explained that complete ozone degradation in a BaTiO₃ packed bed plasma reactor for high energy densities was feasible due to thermally initiated decomposition processes. Also Chae et al. [28] reported that for temperatures above 100 °C, ozone loss processes with BaTiO₃ catalyst were enhanced.

2.2. Plasma light emission triggering photocatalysis

Combining heterogenic photocatalysts with non-thermal plasma proves to enhance VOC and by-product degradation [43]. Among semiconductor photocatalysts (i.e. ZnO, ZnS, CdS, Fe₂O₃, WO₃, etc.), titanium dioxide (TiO₂) is the most active, due to its photo-stability, strong oxidizing power, non-toxicity, chemical and biological inertness, stability, as well as its low cost [53].

Plasma triggered photocatalytic effects are not well understood. Some scientists state that UV wavelengths in the plasma discharge triggers oxidation reactions due to the formation of electron–hole pairs on the catalysts surface [54,55]. Indeed, UV light is produced by non-thermal plasma due to excited nitrogen molecules. Sano et al. [23] reported that in the absence of TiO₂, UV light was emitted in a plasma discharge. The strongest emissions originate from the second positive system (SPS: C₃Π_u → B₃Π_g), which emits photons of 337.1 nm. The first negative system (FNS: B₂Σ_u⁺ → X₂Σ_g⁺) of N₂⁺ emits 391.4 nm. In the presence of TiO₂ no UV light was detected, indicating that these wavelengths were absorbed by the catalyst (Fig. 6).

Other scientists measured no increased UV emission in some plasma discharges [56]. The similar synergetic effects seemed to originate from the direct activation of the photocatalyst by the plasma discharge [23,24]. Chavadey et al. [42] concluded that the catalytic property of TiO₂ is mainly due to the availability of reaction sites and its reducible property. Also Kim et al. [12] proved that UV emission is not always the controlling factor when photocatalyst are introduced. In Ar–O₂ gas streams only visible light is produced (400–850 nm). However, when combined with TiO₂, the synergetic effect was

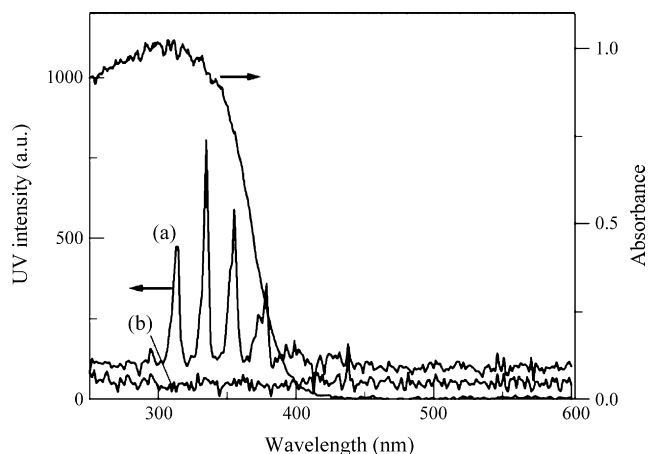


Fig. 6. UV–vis emission spectra of surface discharge plasma observed from the outside of envelope without catalyst (a) and with TiO_2 (b), and the diffuse reflectance spectrum of TiO_2 . Air was passed through a barrier tube with a flow rate of 100 mL min^{-1} , the input power was 8 W [23].

more important than in N_2/O_2 mixtures [12,43]. It can be concluded that activation of the catalyst surface may also be explained by adsorption of high-energy species since metastable N_2^* has an energy of 6.17 eV , while Ar contains about 13 eV . Finally, as already described earlier, a generation of new reactive species on the catalyst surface might also be possible.

3. Environmental applications of plasma catalytic hybrid systems

3.1. Abatement of VOC

Table 1 gives an overview of recently published manuscripts about plasma catalytic VOC removal. From this table it can be concluded that dielectric barrier discharges are most frequently used in recent plasma catalytic research. Most research has been done on inserting heterogeneous catalysts in the discharge. Nevertheless, post plasma catalysis is equally promising for environmental purposes [11]. The main advantages of combining NTP with heterogeneous catalysts are an improvement of energy efficiency and a higher mineralization degree.

The type of VOC pollutant strongly determines the degree of VOC removal efficiency [4]. These variations in removal efficiency are caused by the presence of different functional groups. To illustrate this, reaction rate constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for hydroxyl radicals and C6 hydrocarbons having a varying number of unsaturated bounds, are 4.03×10^{-12} , 3.7×10^{-11} and $1.19 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for C_6H_{14} , C_6H_{12} and C_6H_{10} , respectively. Generally, chlorinated VOCs can be removed with a higher energy efficiency due to the generation of chlorine radical chain reactions initiated by a chlorine atoms detachment. Generally, recent papers on hybrid plasma catalyst technology consider that the energy efficiency tends to increase with increasing initial pollutant concentration [4,20]. Delagrangé et al. [26] concluded that the activity of the catalyst depends mainly on the support used. Kim et al. [7] described the importance of metal loading in catalyst material

during plasma catalytic processes. It was shown that conventional TiO_2 and Ag supported TiO_2 have different roles in the benzene decomposition [7]. TiO_2 is responsible for the initial decomposition of benzene. However, Ag plays an important role in the decomposition of the surface intermediates. It was proven that the higher the Ag loading amount, the better the mineralization degree [7]. Similar conclusions were taken by Kang et al. [54]. The insertion of 10.0 mol\% Bi in TiO_2 catalysts resulted in smaller crystalline structure and an increased hydrophobicity. Wu et al. [53] wrote that doping of TiO_2 with La resulted in increased porosity, uniformity and roughness, again resulting in better adsorption and decomposition of VOC. The conclusion that physical/chemical properties are dominating for the catalytic removal efficiency, is contradictory with processes as described by Kim et al. [7] who reported that the degree of initial conversion was mostly determined by specific input energy, regardless of the type of catalyst. In this study, the catalyst surface area also proved to have little influence on the decomposition efficiency [7].

3.2. Reduction of nitrogen oxides

Non-thermal plasma applications for NO_x emission reduction has been widely studied in the last years [57–61]. However, until today NTP and more recent hybrid plasma catalyst technology has not matured yet to meet 2007 regulations [5].

For these kinds of applications, plasma-facilitated catalysis is most a two-step process which consists of a plasma pretreatment of the exhaust before flow over a lean NO_x catalyst [6,62]. At lower reaction temperatures ($<500 \text{ K}$), the efficiency of selective catalytic reduction (SCR) of NO_x strongly depends on initial NO_2 concentration in the gas stream. About 30–50% of NO_2 in the gas stream greatly enhances the performance of SCR in DeNO_x processes [6,62,63]. However, in real conditions the fraction of NO_2 present in the total NO_x seldom exceeds 5%. The plasma however, converts a part of NO into NO_2 [63,64]. Basically (plasma generated) ozone, hydroxyl radicals and atomic oxygen play an important role in the oxidation of NO to NO_2 . When hydrocarbons are simultaneously treated by the plasma discharge, partially oxidized hydrocarbons and peroxy radicals (RO_2) are generated which react with NO and strongly influence NO_2 formation rates [6,62]. After the pretreatment step, NO_2 reacts over a catalyst while partially oxidized hydrocarbons are consumed during selective catalytic reduction producing CO_2 , N_2 and H_2O [48].

Two main classes of catalysts, zeolites and metal oxides, have been reported to be highly effective for NO_x removal in combination with non-thermal plasma. It was proven that the addition of alkali and alkaline earth species (for zeolites) or transition metal ions (for γ -alumina) enhances catalytic activity [62]. In recent publications both designs, in-plasma catalysis [65,56] and downstream catalysis [6,47,62,64,56], have been examined for NO_x reduction purposes. Niu et al. [66] reported that NO_x conversion by a catalyst-filled dielectric barrier discharge with methane additive was much higher than with plasma alone. The NO_x conversion for pure plasma induced, pure catalyst induced and plasma-catalyst induced reactions

was 24, 25 and 65%, respectively [66]. Also Sun et al. [67] described synergetic interactions in a one-stage plasma-over catalyst reactor between DBD plasma and Cu-ZSM-5 catalyst during C₂H₄ selective reduction of NO_x. Studies however proved that these in-plasma catalytic systems behave similarly to those with the catalyst positioned post plasma. This implicates that the catalytic mechanism does not involve effects such as electric field enhancement or electron impact excitation of the catalyst surface. Instead, stable or metastable species created in the plasma may be central to the catalysis [5].

Okubo et al. [64] reported that plasma pretreatment is not always effective. For higher temperatures (at high energy densities) less ozone is produced in the plasma. Secondly reaction rates of NO/O₂ and NO/OH₂ decrease, resulting in reduced NO₂ formation rates. Finally, during plasma pretreatment, OH radicals may convert the formed NO₂ into HNO₃ [63] and high O₂ levels may lead to a conversion back to NO [64]. For gas temperatures lower than 450 K, ammonium nitrate formation should be considered in order to avoid deactivation of catalysts. It can be concluded that plasma characteristics and heating effects are important parameters in the design of plasma reactors used as a pretreatment technology.

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